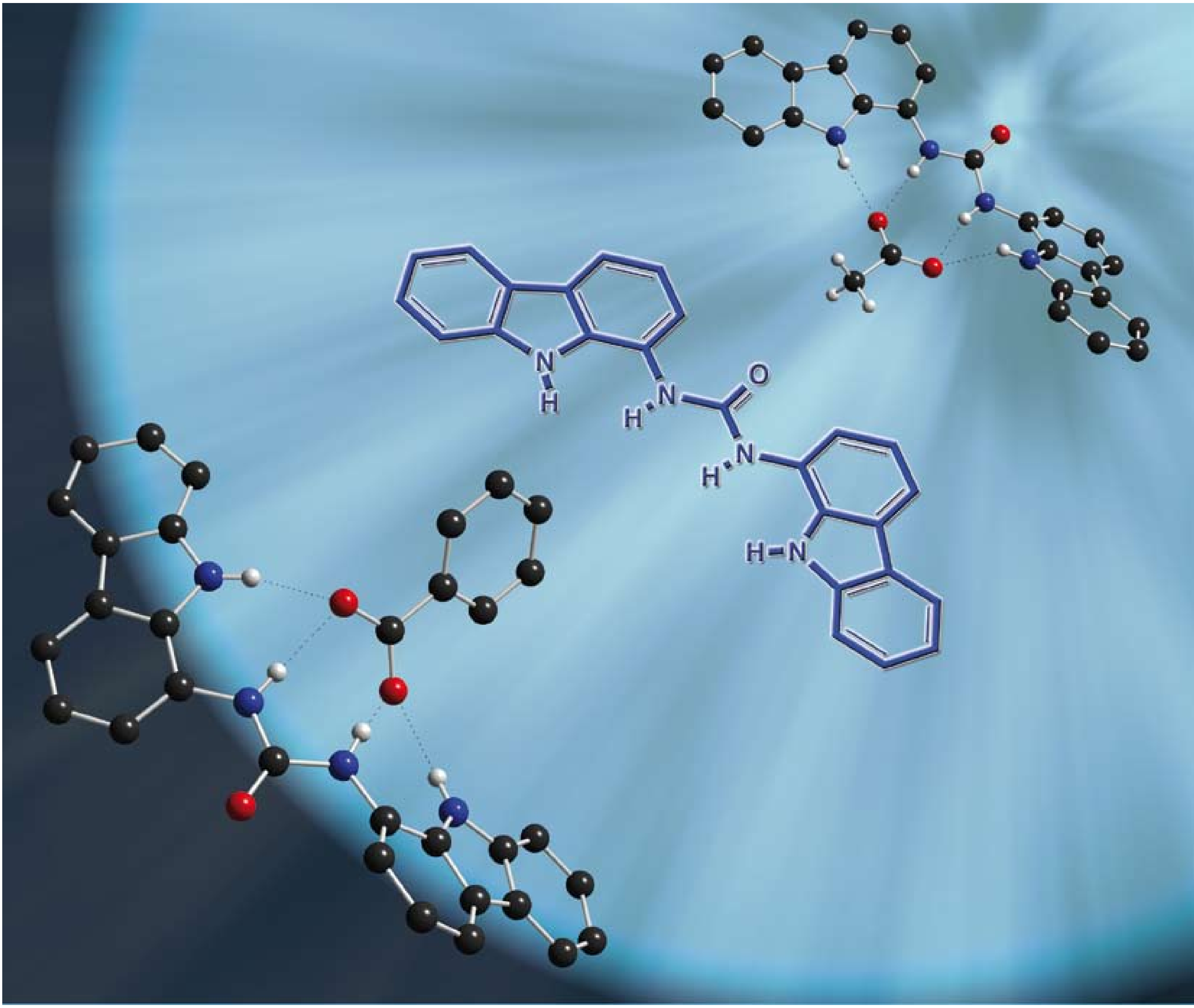
Organic & Biomolecular Chemistry

www.rsc.org/obc

Volume 7 | Number 9 | 7 May 2009 | Pages 1737–1988



ISSN 1477-0520

RSC Publishing

COMMUNICATION
Jennifer R. Hiscock *et al.*
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Chemical Biology
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1477-0520(2009)7:9;1-6

Fluorescent carbazolylurea anion receptors†‡

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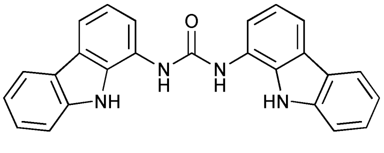
Received 6th January 2009, Accepted 11th February 2009
First published as an Advance Article on the web 20th February 2009
DOI: 10.1039/b900178f

A series of fluorescent carbazolylurea base anion receptors have been synthesised that show a high affinity for oxo-anions (particularly bicarbonate and acetate). The fluorescence of dicarbazolylurea (1) is quenched upon addition of benzoate anions in DMSO–0.5% water.

Our interest in anion complexation[1] has led us to investigate compounds that are easy to make and yet have high affinities and selectivities for anionic guests.[2] Work from the groups of Jeong,[3] Jurczak,[4] Beer,[5] Sessler,[6] Pfeffer[7] and ourselves[8] has shown that indoles, carbazoles, indolocarbazoles and biindoles are effective components of hydrogen bond donating anion receptors.[9] In a recent collaboration with Albrecht, we found that 2,7-disubstituted indoles were effective receptors for carboxylates.[10] Building on this work, we discovered that diindolylurea compounds have very high affinities for oxoanions and selectively bind dihydrogen phosphate in DMSO–water mixtures.[11] In this communication we report the synthesis and anion binding properties of related carbazolylureas (**1–3**). In addition to forming strong complexes with oxoanionic guests, the fluorescence of these easy-to-make receptors is perturbed in the presence of anions, allowing them to be employed as fluorescent anion sensors.[12]

1-Nitrocarbazole was synthesised *via* a modification to a literature procedure (see ESI‡).[13] This was then reduced with hydrogen over 10% Pd/C to afford the 1-aminocarbazole. This compound was then dissolved in a mixture of dichloromethane and saturated aqueous NaHCO$_3$, and one equivalent of triphosgene added to afford the isocyanate in quantitative yield. This compound proved to be very reactive and hence was used immediately. Compounds **1** and **2** were synthesised in 41% and 26% respective yields by addition of a solution of the isocyanate in dichloromethane to a solution of 1-aminocarbazole or 7-aminoindole and triethylamine in chloroform. Compound **3** was prepared in 69% yield by addition of a solution of phenylisocyanate in dichloromethane to a solution of 1-aminocarbazole in dichloromethane.



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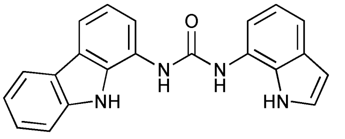

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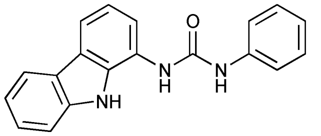

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Anion complexation studies were performed using ^{1}H NMR titration techniques in DMSO-d_6–0.5% water with stability constants obtained from the titration curves using the EQNMR computer program.[14] The results (see Table 1) show that all the compounds bind acetate strongly. NMR titrations with dihydrogen phosphate show strong binding but the titration curves for compounds **1** and **2** show features at 1 and 2 equivalents of anion that cannot be fitted adequately to a binding model (see ESI). Titrations with fluoride caused broadening of the NH resonances in all cases, and thus it was not possible to determine an accurate stability constant. Shifts of the NH resonances suggest weak complex formation (*i.e.* a continuous downfield shift – see ESI for compounds **2** and **3**). Binding studies were also conducted with tetraethylammonium bicarbonate. Strong binding was observed in all cases with stability constants $>10^4$ M^{-1}.

Crystals of the acetate complex of compound **1** were grown by slow evaporation of a DMSO solution of the receptor in the presence of excess tetrabutylammonium acetate.§ The structure (shown in Fig. 1) reveals that the receptor binds acetate *via* four NH···O hydrogen bonds (N1···O2 2.781(2) Å; N2···O2

Table 1 The stability constants (M^{-1}) of compounds **1**, **2** and **3** with a variety of anionic guests (added as tetrabutylammonium salts except bicarbonate which was added as a tetraethylammonium salt) at 298 K in DMSO-d_6–0.5% water as determined by following urea NH resonance adjacent to the carbazole. In all cases 1 : 1 receptor: anion stoichiometry was observed. Errors estimated to be no more than ±15%

Anion	Compound **1**	Compound **2**	Compound **3**
Acetate	$>10^4$	$>10^4$	$>10^4$
Benzoate	5670	5880	3420
Dihydrogen phosphate	[a]	[a]	6140
Chloride	102	139	85
Bicarbonate	$>10^4$	$>10^4$	$>10^4$

[a] NMR titration curve could not be fitted to a 1 : 1 or 1 : 2 receptor:anion binding stoichimetry but indicates strong binding.

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† Dedicated to Professor Roeland Nolte on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Experimental details, ^{1}H and ^{13}C NMR spectra, NMR titration curves and fluorescence spectra. CCDC reference numbers 715669 and 715670. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b900178f

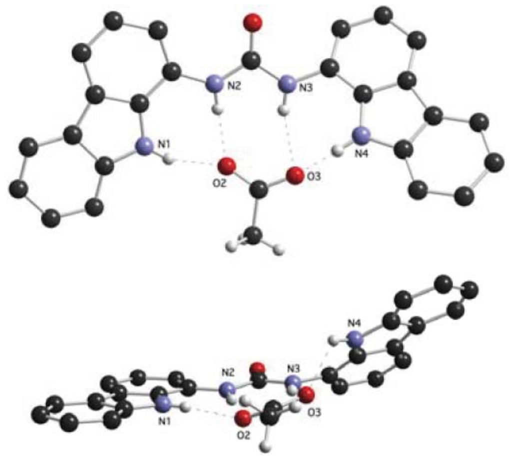

Fig. 1 Two views of the X-ray crystal structure of the acetate complex of receptor **1**. The tetrabutylammonium counter-cation and selected hydrogen atoms have been omitted for clarity.

2.809(2) Å; N3 $\cdots$ O3 2.926(2) Å; N4 $\cdots$ O3 2.820(2) Å). One of the carbazoles is in the plane of the urea group whilst the other twists out of plane by 39.9°.

Crystals of the benzoate complex of compound **1** were grown by slow evaporation of a DMSO solution of the receptor in the presence of excess tetrabutylammonium benzoate.¶ The unit cell contains two crystallographically distinct benzoate complexes which adopt similar conformations. One example is shown in Fig. 2. As with the acetate complex, in both benzoate complexes one of the carbazoles is in the plane of the urea whilst the other is twisted out of plane by 37.1° or 43.0°. Each benzoate anion is bound by four hydrogen bonds in the range N $\cdots$ O 2.762(5)–2.996(5) Å.

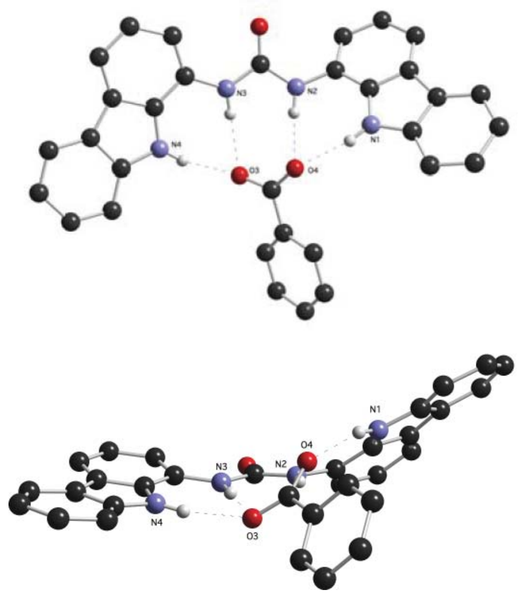

Fig. 2 Two views of the X-ray crystal structure of one of the two crystallographically distinct benzoate complexes present in the unit cell of the tetrabutylammonium benzoate complex of receptor **1**. Tetrabutylammonium counter-cations and selected hydrogen atoms have been omitted for clarity.

In order to investigate the ability of receptors **1–3** to act as luminescent sensors, fluorescence studies were performed in a DMSO–0.5% water mixture. Under these conditions receptor **1** shows an intense fluorescence emission ($\Phi = 0.549$) with maxima at 363 nm and 376 nm when excited at 270 nm. As shown in Fig. 3 upon addition of increasing amounts of tetrabutylammonium benzoate, a selective quenching of the fluorescent emission was observed ($I_{\text{res}} = 10\%$).

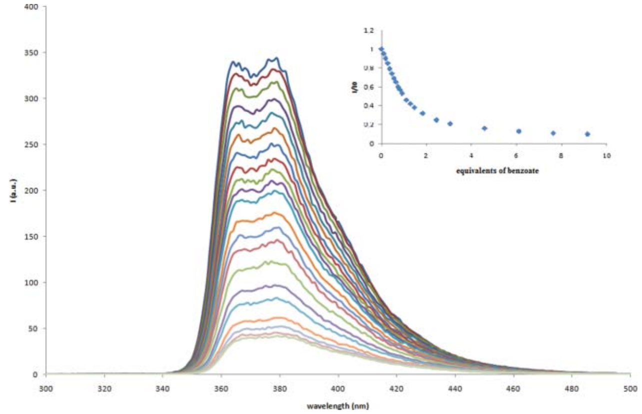

Fig. 3 Fluorescence quenching of receptor **1** in DMSO–0.5% water upon addition of increasing amounts of tetrabutylammonium benzoate.

Upon addition of the tetrabutylammonium salts of acetate, fluoride chloride and dihydrogen phosphate and the tetraethylammonium salt of bicarbonate, less dramatic effects were observed (Fig. 4). In fact, only acetate caused a partial quenching of the emission ($I_{\text{res}} = 50\%$) while a stronger quenching upon addition of fluoride was observed but only when an excess of anion was added (more than three equivalents), which may be indicative of deprotonation.[15] A slight perturbation of the fluorescence emission of **1** was observed in the presence of dihydrogen phosphate ($I_{\text{res}} = 68\%$) and bicarbonate ($I_{\text{res}} = 73\%$). Chloride did not effect the emission of the system. The trend in fluorescence quenching is similar to that found for the stability constants by ^{1}H-NMR titrations with the exception for benzoate. This may be due to a π–π interaction in the excited state between the aromatic electrons of the carbazole moieties and the substrate.

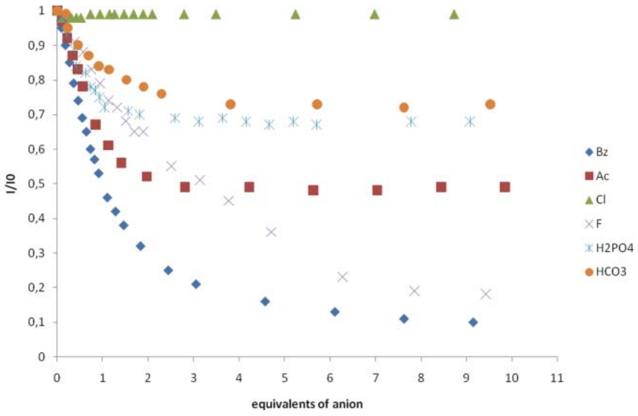

Fig. 4 Effect of increasing anion concentration upon the relative fluorescence emission of receptor **1** in DMSO–0.5% water.

Similar but less pronounced quenching effects caused by benzoate were observed with receptor **2** (Φ = 0.562 and **3** (Φ = 0.501) (see ESI). Thus, under these conditions receptor **1** acts as a selective ON–OFF fluorescent sensor for benzoate.

Compounds **1–3** are easy-to-make analogues of the diindolylureas, binding acetate and bicarbonate strongly. The fluorescence of compound **1** is selectively quenched by benzoate. We are continuing to explore the anion complexation and sensing properties of indole and carbazole ureas, and the results of these studies will be reported in due course.

Acknowledgements

P.A.G. thanks the EPSRC for a DTA studentship (JRH). C.C. would like to thank the Italian Ministero dell'Istruzione, dell'Università e della Ricerca Scientifica (MIUR) for financial support (Project PRIN-2007C8RW53).

Notes and references

§ Crystal data were collected on a Bruker Nonius KappaCCD with a Mo rotating anode generator; standard procedures were followed. Crystal data for compound **1**·tetrabutylammonium acetate: $C_{43}H_{57}N_5O_3$, $M = 691.94$, $T = 120(2)$ K, monoclinic, space group $P2_1/n$, $a = 11.0933(2)$, $b = 26.7833(6)$, $c = 13.2013(3)$ Å, $\beta = 98.0560(10)°$, $V = 3883.60(14)$ Å^3, $\rho_c = 1.183$ g cm^{-3}, $\mu = 0.075$ mm^{-1}, $Z = 4$, reflections collected: 40088, independent reflections: 8914 ($R_{int} = 0.0815$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0674$, w$R_2 = 0.1354$, R indices (all data): $R_1 = 0.1274$. w$R_2 = 0.1613$.

¶ Crystal data for compound **1**·tetrabutylammoniuma benzoate: $C_{48}H_{59}N_5O_3$, $M = 754.00$, $T = 120(2)$ K, triclinic, space group $P1a = 10.980(5)$, $b = 13.774(5)$, $c = 15.173(5)$ Å, $\alpha = 68.760(5)°$, $\beta = 85.232(5)°$, $\gamma = 81.541(5)°$, $V = 2114.5(14)$ Å^3, $\rho_c = 1.184$ g cm^{-3}, $\mu = 0.074$ mm^{-1}, $Z = 2$, reflections collected: 44837, independent reflections: 9728 ($R_{int} = 0.1052$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0661$, w$R_2 = 0.1368$, R indices (all data): $R_1 = 0.1190$. w$R_2 = 0.1589$.

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